

THE ANALYST.

NOVEMBER, 1893.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

THE usual Monthly Meeting of this Society was held on October 4th, at the rooms of the Chemical Society, Burlington House. In the absence of the President, Mr. Otto Hehner occupied the chair.

The minutes of the last meeting were read and confirmed.

Mr. George Rudd Thompson, F.I.C., 57, Dock Street, Newport, Mon., was proposed as a Member.

The following gentlemen were duly elected: As Member, Mr. Wallis Jenkins, Hull. As Associates, Mr. John B. Ashworth, Liverpool, and Mr. Benjamin Watmough, Leeds.

The following paper was then read by the author:

DISTINCTION BETWEEN IRON PYRITES AND OXIDE OF IRON IN THE COMMERCIAL ANALYSIS OF MINERAL PHOSPHATES.

BY H. H. B. SHEPHERD.

WHEN, in 1891, the Glaser method for the determination of oxide of iron and alumina in phosphates was under consideration by a conference of chemists assembled at the instance of the Chemical Manure Manufacturers' Association, the question as to the acid to be employed as solvent came under discussion, general exception being taken to the use of nitrohydrochloric acid, as directed by Glaser, on the ground that iron, existing in the form of pyrites, would thereby be improperly included in the determination.

Considerable differences between the results of English and continental chemists have lately come to my knowledge which are clearly traceable to this cause, English chemists determining, as a rule, the iron and alumina soluble in hydrochloric acid, and German, French, and Belgian chemists that soluble in a mixture of nitric and hydrochloric acids.

The view taken by most English chemists is very clearly expressed in the following extract from a paper by Dr. Bernard Dyer (*Chem. News*, liii. 51):

"It may have been noticed at the outset I mentioned hydrochloric acid as a solvent, and this suggests a point that may be productive, and often *is* productive, of analytical discrepancies. Certain phosphates, as is well known, contain iron pyrites. It is not fair to regard the iron in pyrites as oxide of iron; and hydrochloric acid has the advantage of not dissolving up the pyrites, but leaving it amongst the silicious

matter. The solution contains only the iron existing as oxide (or phosphate). The iron present as pyrites may be determined by igniting the sand and treating it with hydrochloric acid, in which the iron is then of course readily soluble, and may be easily determined.

"But no analysis of a phosphate should include in the term 'oxide of iron,' the iron that is present as pyrites.

"If nitric acid be added to the original solvent, the *whole* of the iron passes into solution, and is all included as 'oxide,' unless, of course, a separate determination of pyrites be made, and a deduction made for it.

"If the pyrites is not shown separately in the analysis of a phosphate which contains it (such as the Carolina river phosphates), the statement ought to be, to avoid misunderstanding, either—

"Oxide of iron (exclusive of iron as pyrites), x.x per cent.,

"or—

"Oxide of iron (inclusive of iron existing as pyrites), x.x per cent.

"But it is far better to state the pyrites and oxide of iron separately, that there may be no confusion. The point is important not merely for avoiding discrepancies, but as materially affecting the apparent value of a phosphate; for iron pyrites in a phosphate is by no means the objectionable constituent that oxide of iron is."

I must acknowledge my indebtedness to my friend for this somewhat free use of his paper. It possesses, however, this special interest, viz., that it was written as a contribution to the discussion of the subject upwards of seven years ago, and, as an expression of opinion on the pyrites question, has remained unchallenged by English chemists, so far, at any rate, as published papers are concerned, ever since.

I may mention, however, in passing, that Mr. W. W. Mallon proposed at about the same time (*Chem. News*, liii. 85) the adoption of dilute sulphuric acid as the solvent, in order to imitate as nearly as possible the actual superphosphate manufacture; but this, though possibly of interest from the point of view of the action of the solvent upon the clay usually present, does not, if considered as an alternative to hydrochloric acid, affect the point at issue. There can be no doubt that amongst most English chemists a decided opinion has been formed against the inclusion of the iron of pyrites in these determinations, based upon its insolubility in the process of superphosphate manufacture, but it does not appear that the distinction between this form of iron and iron in other combinations has hitherto been considered to the same extent on the continent. In none of the published processes can I find any special reference to the question of pyrites, and I can only infer, from the general directions given for the use of nitric acid, that its inclusion is intended.

I have been informed, however, that an attempt at justification has lately been made by a German chemist in a communication to his clients, on the grounds that oxides of nitrogen are present in small quantities in the chamber acid used by superphosphate manufacturers, and though I confess to have been biased against this as a serious argument, I have, nevertheless, endeavoured to give it impartial consideration. Now, Lunge ("Sulphuric Acid and Alkali," p. 466) gives a table on the authority of Kolb, showing the amounts of nitrous and nitric acids present in chamber acid under different circumstances, from which I gather that under normal conditions the sum total of both nitrous and nitric acids does not amount to *more* than about 0.03 per cent.

I have myself examined a good many samples of chamber acid, and am convinced that under normal working conditions the total amount of nitrous and nitric acids cannot be regarded as more than a trace. Frequently it is only sufficient to give the faintest possible reaction with ferrous sulphate. The following are some results which I have recently obtained on testing the acid from the various parts of a set of chambers with towers in good working order :

Total nitrosity in terms of N_2O_5 .				
No. 1 chamber	...	...	...	0.002
No. 2 „	...	...	...	too small to determine
No. 3 „	...	...	...	0.002
No. 4 „	...	...	...	0.001
Denitrated acid from the Glover tower	...	...	...	0.003

The amount, of course, fluctuates within certain limits, but I maintain that the average nitrosity is quite insufficient to act upon the pyrites in the way alleged.

The following tests were recently made in samples of acid used for dissolving, obtained from different Works :

Total nitrosity in terms of N_2O_5 .				
No. 1 Works	...	...	...	0.022
No. 2 „	...	...	...	0.004
No. 3 „	...	...	...	0.003

I have, however, carried the inquiry a step further by submitting the matter to an actual practical test. At the works with which I am connected we lately received a parcel of South Carolina river phosphate of the following analysis :

Phosphoric acid	...	...	...	27.37
Iron in form of pyrites	...	...	...	0.77

With this material I made an experimental superphosphate mixing, on a manufacturing scale, using equal parts of phosphate and chamber acid of 110° Tw.

The superphosphate showed on analysis the following results :

Total phosphoric acid	...	...	...	14.49
Iron in form of pyrites	...	...	...	0.42

Now, in order to compare the pyrites iron found unaltered in the superphosphate with that originally present in the raw phosphate it is necessary to make a correction for the decrease in weight due to loss of carbonic acid, water, etc., resulting from the mixing.

Of the two ways of determining this loss, viz., by weighing the resulting superphosphate, or by calculation from the total phosphoric acid found in it, I prefer the latter as being more exact, and this gives a loss in the present instance of 5.60 per cent.

The comparison, after making the necessary correction, will therefore stand as follows :

Pyrites iron in the materials before mixing	...	0.41
„ „ „ after „	...	0.42

The plea advanced in Germany appears, therefore, to be groundless.

It is only fair, however, to state that I have succeeded in dissolving a small proportion of the iron of pyrites in a phosphate by chamber acid, but only under conditions that could never possibly occur in practice. By long digestion in a very large excess of an acid of unusually high nitrosity, and at a higher temperature than occurs in the actual manufacture, I actually effected the solution of 0.19 per cent. of pyrites iron.

Many chemists may not be aware how seriously the trade is affected by differences due to the divergence in practice referred to.

It is the custom for sellers to guarantee a maximum percentage of oxide of iron and alumina, with the proviso that, should the guarantee be exceeded, an allowance shall be made of two units of phosphate of lime for every such unit of oxide of iron and alumina in excess of the guarantee. In some cases, however, and notably when French or American phosphates are dealt in, the guarantee goes even beyond this. A maximum of 3 per cent. is guaranteed with compensation as above up to 4 per cent., but should this limit be exceeded buyers have the option of rejecting the entire cargo. It is easy to see what important issues may therefore depend upon the question of the exclusion or inclusion of the iron of pyrites in the determination. A phosphate containing but 3 per cent. of oxide of iron and alumina may by the inclusion of the iron of the pyrites be brought over the 4 per cent. limit, with the result of the rejection of a cargo involving consequences amounting possibly to thousands of pounds.

We have to bear in mind in these questions that the chemist's certificate is required, principally, if not solely, as a basis of price between buyer and seller, and that the want of a uniform system renders one party liable to gain an unfair advantage at the expense of the other.

As it is so clearly desirable that we should endeavour to come to an understanding with our continental friends upon the subject, I should be very glad to receive any assistance in the way of suggestion or otherwise that might help towards the attainment of this end.

DISCUSSION.

Mr. Otto Hehner said that, as there were several members of the Society present who had a wide experience in the matter brought forward by Mr. Shepherd, he hoped they would take part in the discussion. As to the international arrangement which had been suggested, he should be pleased to see it brought about; but, in any case, the publication of the matter would doubtless tend to remove the discrepancies which existed at the present time.

Mr. Hermann Voss said that as a manufacturer he would not discuss the more scientific part of the matter, but perhaps he might be permitted to say a few words about the commercial side of the question. As had been stated in the paper, it was a very important question, not only for the merchant, the buyer, and the seller, but also for the manufacturer in the end, because on the correctness of the determination of iron and alumina depended the calculation as to the mode of manufacture, and also the profit or loss on the manufactured article, because the manufacturer had to

guarantee the presence of so much soluble phosphate in the superphosphate, and if the first determination of iron and alumina in the phosphate was not quite correct, or was misleading, he would not be correct in his calculation as to what was the result he might expect in the manufactured article, and it might ultimately turn out that he would have to pay for deficiency. He was in a position to state that recently the differences among results alluded to in the paper had been very great. At a meeting of chemists and the trade an endeavour had been made to find out a way by which more uniform results could be obtained. He thought that the meeting of chemists held in London had been productive of good results, inasmuch as it brought the results of the English chemists nearer than they were before. But since the introduction of the Glaser method, and the various modifications thereof, it seemed to have had the effect of again bringing out differences not only between the results of continental chemists, but also between the results of English chemists, and he believed the tables which he had had prepared would show that the differences in the results in the iron and alumina determinations in commercial phosphates were very great.

OXIDE OF IRON AND ALUMINA TESTS IN RECENT SHIPMENTS OF SOMME PHOSPHATES.

Cargo.	Chemist.	Oxide of iron and alumina combined. Total.	Oxide of iron.	Alumina.
No. 1	English	2.20	1.23	0.25
	French	1.48		
No. 2	English	3.60	1.35	0.63
	French	1.98		
	German	3.24		
No. 3	German	2.64	1.23	0.21
	"	3.85		
	French	1.44		
	English	2.90		
No. 4	French	1.54	1.29	0.25
	English	2.62	1.10	1.52
	"	2.70		
No. 5	German	3.91	1.60	0.89
	"	3.67		
	Belgian	2.33		
	French	2.49		
No. 6	French	2.28	1.36	0.92
	English	3.15		
	"	3.17		
No. 7	English	3.95	1.76	2.13
	"	3.89		
	French	2.93	1.77	1.16

OXIDE OF IRON AND ALUMINA TESTS IN RECENT SHIPMENTS OF OSSO PHOSPHATES.

Cargo.	Chemist.	Oxide of iron and alumina combined. Total.	Oxide of iron.	Alumina.
No. 1	French	3.98	2.36	1.62
	Belgian	3.72		
No. 2	English	5.96	1.79	1.63
	Belgian	4.74		
	French	3.42		
No. 3	English	4.97	3.06	1.84
	"	5.40		
	Belgian	3.75		
No. 4	French	4.90	2.50	3.43
	English	5.50		
	"	6.10		
	Belgian	3.40		
No. 5	English	5.93	2.86	3.08
	"	5.94		
	Belgian	4.97		
	"	4.20		
No. 6	English	4.76	2.02	0.71
	Belgian	3.23		
No. 7	French	2.73		
	English	4.03		

OXIDE OF IRON AND ALUMINA TESTS IN RECENT SHIPMENTS OF RIVER PHOSPHATE.

Cargo.	Chemist.	Oxide of iron and alumina combined. Total.	Oxide of iron.	Alumina.	Iron pyrites determined separately.
No. 1	German	2.30			0.52
	"	2.65			0.23
No. 2	English	1.81	1.14	0.67	2.46
	German	3.27			
No. 3	German	2.95	1.50	1.45	0.26
	"	2.84	2.14	0.70	0.39
No. 4	English	2.02	0.60	1.42	0.52
No. 5	English	2.16	1.45	0.71	1.57
	"	2.32	1.70	0.62	
	"	3.00			
No. 6	English	2.19	1.31	0.88	0.84
No. 7	English	1.62	1.26	0.36	2.63
	"	1.43			
No. 8	English	2.32	1.11	1.21	1.11
	"	2.30			
No. 9	English	1.60	1.24	0.36	2.61

At that meeting it was said that the results should not vary more than a half per cent., and it would be quite enough if in a contract for phosphates it was stated that if a difference of a half per cent. existed the matter should be referred to a third chemist. The figures in the tables sometimes amounted to as much as 2 per cent., which could not be due to variation in the sample. It could only be traced to the different methods employed. He thought it would be self-evident that the trade, the manufacturer, as well as the merchant, were very often at a loss to know where the truth really lay. He did not know who was right and who was wrong, but he thought that it was in the interests of science, especially of the science of chemistry, that such serious differences should disappear. The greatest difference occurred in phosphates sold in either France or Belgium, because they were sold on the mean of the results obtained by French or Belgian chemists, and on those obtained by English chemists, the differences sometimes amounting to over 2 per cent. As the author of the paper had said, there was a guarantee of 3 per cent., with a maximum of 4 per cent., and if this maximum were exceeded it happened that cargoes were thrown on the hands of the seller, the sums involved sometimes amounting to thousands of pounds. As an illustration, he would refer to one case where the average percentage of iron and alumina amounted to 4.05. The maximum guarantee was exceeded, and consequently the buyer had a right to throw up the whole cargo, which consisted of 2,500 tons. The price of the phosphate had dropped 12s. to 15s. a ton, and there was a further difference claimed of 5s. or 6s. a ton. Finally the matter was settled by an allowance of £2,500—for the sake of 0.05 per cent. This sort of thing only happened on rare occasions, and he was quite sure that not many buyers would be found who would, for the sake of 0.05, claim a difference of £2,500. With regard to iron pyrites in phosphates, he believed, as is shown in the paper, that manufacturers need not fear the presence of such pyrites, and therefore it should not be quoted amongst the noxious ingredients of the phosphate. It would be found that in one of these tables there was an analysis by an English chemist who obtained 1.81 of iron and alumina, whilst a German chemist found above 3 per cent. in another sample of the same cargo. The disparity could not be explained by the difference in material, or by errors in analysis; it could only be explained by the custom of employing different methods of analysis. Although attempts had been made to get continental chemists to adopt the same method as that employed by English chemists, the former seemed to think that their method was a better and a more correct one; and as merchants here bought phosphates on the continent, they had to accept the figures. He was quite convinced that if chemists in this country would set the ball rolling, the matter would be seriously discussed on the continent, and the best method of analysis would then be arrived at.

Mr. John Hughes confirmed what had been said by Mr. Shepherd. From the remarks which had fallen from Mr. Voss he gathered that it must be a practice, at least among certain chemists on the continent, to determine and include the iron of the pyrites in the total oxide of iron, without making any distinction, and if that was the case, the members of the Society should take the opportunity of stating very plainly that, among English chemists, it was not the practice to recognise the presence of pyrites as in any way injurious in the manufacture of superphosphate.

He himself had never included the iron of the pyrites when reporting his determinations of iron. He had had in the past a great deal of experience in the matter of the treatment of river phosphates containing pyrites during the time he was associated with Messrs. Lawes and Co., and he had ample opportunity of testing whether or not the pyrites was affected by the action of the acid. He found that no appreciable action took place during the mixing, as mentioned by Mr. Shepherd; but if chamber acid were taken, and the sample was treated with an excessive quantity of this acid, in some cases it was possible to oxidize a considerable portion, if not the whole of the iron of the pyrites; but in the manufacture of superphosphate that was not the case, the conditions being different, and the phosphate, and not the acid, being in excess. Regarding what Mr. Voss had said in reference to the matter of variation in the results obtained by English, as compared with those obtained by continental chemists, he would like to mention that at a meeting of manure manufacturers some years ago he took up the same line of suggestion, namely, that when gentlemen of business reduce to writing certain prices for the sale of certain products they should themselves take a little trouble, first of all, to find out what the limits really ought to be as regards this objectionable iron. He had frequently been called in to assist in disputed cases; but had he been called in to advise, before the contract was made, no difficulty would have arisen. As regarded the case mentioned by Mr. Voss, had the sellers of the phosphates taken the trouble to have the cargo carefully tested, not once, but several times, they would have been able themselves to know how far they could go in guaranteeing the quality of the phosphates as regarded the presence of iron and alumina. He therefore suggested that whilst chemists should, of course, endeavour to be as accurate as possible in their determinations, it was only fair that the manufacturers themselves should take a little trouble, and give the chemist an opportunity of making an analysis and of saying whether or not they could guarantee the materials to be of a certain quality.

Dr. Bernard Dyer also confirmed what had been said by the author of the paper. He was of opinion that the confusion between oxide of iron and iron pyrites ought long before now to have been done away with. On the continent it was unfortunately the practice to work more by stereotyped methods. For example, a process for the determination of oxide of iron in phosphates was proposed at a convention of agricultural chemists, and it probably did not occur to anyone present that some phosphates contained pyrites. The process began with the adoption of nitric acid as a solvent, simply because it was a useful solvent, for quite another purpose, viz., for determination of phosphoric acid by molybdenum. The process was then adopted formally and officially, and every chemist in Germany worked by it, and when he came across a phosphate containing pyrites he was bound hand and foot. He had to follow out the prescribed process; he used nitric acid as a solvent, and obtained a result which was altogether wrong. The fact that pyrites was not acted upon to any appreciable extent in superphosphate making, which formed the backbone of Mr. Shepherd's paper, was brought home every day to analysts who had to deal with superphosphates made from phosphates containing pyrites, for they constantly found in such superphosphates pyrites in an unchanged state. Mr. Shepherd's figures showed that practically the whole of the pyrites was left unacted

upon by chamber acid. The suggestion made by Mr. Hughes to the effect that more explicit statements should be made in contracts would be a very desirable one to follow. It surely ought not to be difficult to express in a contract that the oxide of iron and alumina clause should not refer to iron that existed in the form of pyrites. This plain stipulation should be put into the contract, and the chemist who had to carry out the analysis, whether here or abroad, should have that placed before him in writing at the time he received the sample. Confusion would then not occur. He himself had been of opinion all along, and he had expressed it frequently, that the main differences that occurred between different determinations of oxide of iron and alumina were due, mostly, to the employment of different solvents. He thought that when the iron and alumina had got into solution the differences which might legitimately occur in determining their quantities need be very small. In some phosphates a great deal of clay or kindred aluminous mineral was present, and if merely dilute hydrochloric acid were used the clay was scarcely touched, although the mineral was readily attacked by chamber acid. Evaporation to dryness, with a proper quantity of strong hydrochloric acid, produced practically the same result as the chamber acid. He hoped that Mr. Shepherd's paper, and the discussion on it, would find its way into the analytical journals all over the continent, and that discussion would thereby be aroused abroad as well as at home.

Mr. Shepherd, in reply, said he was pleased to find there had been no adverse criticism on his paper, and thanked Dr. Dyer and Mr. Hughes for their emphatic expressions of opinion in support of the English system of analysis. He thought that Dr. Dyer's surmise as to the origin of the use of nitric acid in Germany was very probably correct, viz., that it was taken in the first instance simply on account of its general use as a solvent for analytical purposes, and that the practice having been begun, was continued, quite irrespective of the action of the acid upon the pyrites, which seemed, indeed, until attention was recently directed to it, to have been altogether overlooked. In face, however, of the present attitude of continental chemists on the matter, he did not think that Mr. Hughes' suggestion to insert a clause in contracts directed against returning pyrites iron as oxide of iron could be carried out. Merchants themselves, moreover, had not always the requisite knowledge at their command to enable them to form a correct opinion upon a purely chemical question, and their interests as buyers and sellers were conflicting. It was only natural, therefore, that they should appeal to chemists for that guidance which it seemed to him particularly within their province to give. No doubt if English chemists expressed themselves freely and forcibly upon the subject, their views would receive attention on the continent. English chemists, however, it seemed to him, stood somewhat at a disadvantage in comparison with their continental brethren, inasmuch as their views could only be expressed individually, and he thought the time was approaching when the continental plan of annual conventions would have to be tried in this country. He suggested that if the Society of Public Analysts or any other recognised body of chemists would take steps in that direction they would earn the gratitude of the mercantile community.

Mr. Richmond then read the following paper :

THE DISCRIMINATION BETWEEN ABNORMAL AND ADULTERATED MILKS.

By H. DROOP RICHMOND.

THE long-continued drought and consequent scarcity of fodder during the summer of 1893 have not been without influence on the composition of milk, and cases have occurred in which the figures given on analysis by genuine milks have fallen below the limits recommended by the Society of Public Analysts to a notable extent. As some of these cases have been used for defending adulteration cases, public analysts may be influenced to adopt a larger margin of safety in interpreting their analytical results, and as a consequence allow larger amounts of adulteration to pass unnoticed. I have collated the results obtained during the present summer, in order to see whether any difference exists between abnormal and adulterated samples.

Though my samples have been neither very abnormal nor as strictly authenticated as some of the samples which have been in the hands of other analysts, I am induced to bring my results before the Society, on account of recent evidence given in court by chemists who are popularly looked upon as authorities on milk-analysis, in which the statement was made that it is impossible to distinguish between abnormal and adulterated samples. As I have had the opportunity of examining comparatively few abnormal samples, I cannot traverse this statement, but I have some evidence that it can be done.

I class as abnormal all samples which fall below the limits of the Society, and divide them into two classes : (1) Those deficient in fat, and (2) those deficient in solids-not-fat.

Class 1. If an analyst finds a sample low in fat, it may be due to three causes :

- (1) Abnormal milk.
- (2) Wilful adulteration.
- (3) Separation of cream during delivery.

It has been decided by the Court of Appeal that a milk-seller is bound to deliver milk as it comes from the cow, and therefore, by this decision, the third cause comes under the Sale of Food and Drugs Act. A suggestion that this might have occurred is manifestly not a good defence, though doubtless if the defendant adduced evidence that this had actually occurred through no gross negligence on his part, no magistrate would impose the maximum penalty ; a defence of this kind would throw no discredit on the public analyst, and after the Lord Chief Justice's ruling he would not be justified in making allowance for this. The defence recently made, that a part of the cream is churned into butter during delivery, is similarly rendered invalid ; indeed, I have found in some thousands of experiments that no appreciable amount of fat is thus removed from the milk by this cause, even in the hottest weather.

It is only necessary to distinguish between adulteration and abnormality. There exists at present, to our knowledge, no method of conclusively deciding between these two ; it is a general, but not universal, rule that low fat in genuine milks is accompanied by low solids-not-fat, and as, moreover, the removal of fat increases the solids-

not-fat, a low fat with high solids-not-fat would give considerable evidence of removal of cream. Any specific gravity of 1.033 or upwards with a low fat is suspicious. As the cream removed contains the larger fat globules, careful microscopical examination will also assist, but the micrography of milk is too imperfectly known to admit of great weight being attached to this evidence. It is perhaps premature to speak of chemical evidence, though the solids-not-fat of separated milk differ to a small extent from those of whole milk. When milk is run through a separator, a thick slime is deposited on the sides of the drum, and this by no means consists wholly of dirt; it is possible that by submitting suspected samples to centrifugal action this slime could be separated and estimated, and from a deficiency of this the presence of separated milk might be presumed.

I may add that the past season has not been characterized by an abnormal lowness in fat, and at the present time I am unable to find any samples with less than 3 per cent. of fat.

Class 2. The known constituents of the solids-not-fat are milk, sugar, proteids (of which casein and albumin are the best known, though others have been described), and salts. The proportion of these is given by Vieth as sugar : proteids : ash = 13 : 9 : 2. My experience shows that this estimate is a very near approach to accuracy.

The Society of Public Analysts in their limit take no account of the separate constituents of the solids-not-fat, but group them together as a whole. Samples do occur which contain less than 8.5 per cent. of solids-not-fat, and these have been specially noticed this summer. Doubtless the cry will be now raised that the time has come to modify these limits. To lower the limit to such a figure as would, while covering the very rare cases of abnormal milk, allow a considerable average adulteration, and would be an act of cowardly betrayal of the honest milk-dealers, who, I venture to think, do not form a minority. It would also play into the hands of unscrupulous tradesmen, and stultify the profession of analytical chemistry.

I have endeavoured to see if the abnormality of these low milks extends further than a deficiency of solids-not-fat. Before the days of Wanklyn, it was the custom to examine the milk more fully than is now done, and to estimate sugar, proteids (collectively or individually), and ash. In my experience the most constant figure in normal milks is the proportion of the ash to the solids-not-fat, which averages 8.3 per cent. It very rarely exceeds the limits of 8.0 to 8.5; in cases of low solids-not-fat this proportion has been disturbed, and the ash has borne a higher ratio to the solids-not-fat. In no case has the percentage of ash in the milk fallen below 0.7 per cent., even in milks notably below the limit. In an adulterated milk containing (say) 8.0 per cent. of solids-not-fat, the ash would be usually lower than this—about 0.66 per cent.; this difference is small, but as the ash is capable of being estimated with great accuracy, it is significant. Other observers have found the same thing; thus Lloyd (*Journ. Chem. Soc.*, 328, 201) finds an average of 0.78 per cent. of ash in a series of abnormal milks as low as 7.5 per cent. of solids-not-fat, and Lowe (*ANALYST*, xviii., 6) 0.94 per cent. of ash in a milk containing 6.0 per cent. of solids-not-fat; De Hailes finds a low ash in one sample (*ANALYST*, xviii., 7), but as his analyses

are very far from agreeing with the formula of Hehner and Richmond, we are justified in considering his work unreliable. Of course, any mineral additions to the milk increase the ash, but there would be no serious difficulty in detecting these in a good many cases, still it cannot be done with certainty in all. The ash of milk is free from carbonates and borates, and (practically) sulphates; the soluble ash is about 30 per cent. of the total ash. Were a milk of low solids-not-fat with a normal ash found, and the soluble ash found to be excessive, of marked alkaline reaction, or containing borates or sulphates in notable amount, the sample may safely be condemned.

In a previous paper I have stated that the deficiency in abnormal milks lies chiefly in the milk sugar; this I have found to be generally true in samples examined this year. The proteids do not decrease to a marked degree; it will be useful in cases of doubt to estimate these. I cannot, however, lay very great stress on these determinations, because not only is the inaccuracy somewhat uncertain, but my experience is limited to about a dozen samples. I am inclined to think that a determination of the total nitrogen is useful, any quantity below 0.5 per cent. being very suspicious. I may incidentally point out that the most reliable data in the analysis of decomposed samples are total nitrogen, ash, and, of course, fat, provided always that a fair average sample can be obtained.

There is one other property of milk which may afford considerable evidence of adulteration—the absence of ~~nitrate~~ nitrates in genuine milk. From evidence given in police courts, it seems that the farmer is responsible for nearly all the adulteration detected; since, from the analysis of numerous water supplies on farms, I find that considerably over half the farms of England are supplied with water containing appreciable amounts of nitrates, there is a great probability that adulteration may be detected by finding nitrates in the milk. A method of detecting nitrates which I have found successful, and which Boseley and I have previously roughly described, is this: Place a small quantity of diphenylamine at the bottom of a porcelain basin, and add to it about 1 c.c. of pure (about 97 per cent.) sulphuric acid; allow a few drops of the serum, obtained by adding a little acetic acid to the milk and warming, to flow down the sides of the basin and over the surface of the acid. If a blue colour develops in the course of ten minutes, though it may be faint, it shows the presence of nitrates; after ten minutes a reddish-brown colour is always developed from the action of the acid on the serum. I have detected the presence of nitrates in a milk purposely mixed with 5 per cent. of water, containing 5 parts per 100,000 of nitric acid, and in two cases where I have found nitrates, I have been able to prove the addition of water by other means. One sample which was watered did not contain nitrates, and in this case I examined the water supply and found it free from nitrates.

In conclusion, I think it right to state that abnormal samples occurred in June, July, and August of this year; but now the quality of milk in all parts of the country has greatly improved, and is at least as high, if not higher, than last year. In my opinion no justification exists for making any allowance for meteorological vagaries.

DISCUSSION.

Dr. Bernard Dyer remarked that Mr. Richmond did not seem to be aware of the fact that a number of years ago Mr. Hehner had proposed the use of

diphenylamine as a test for nitrates in milk with a view to detecting the addition of water.

Mr. Richmond, replying to Dr. Dyer, said that Mr. Hohner had on several occasions told him that he had not been able to make the test work well; and, therefore, he (Mr. Richmond) had thought it desirable to fully describe the mode of manipulation which had given good results.

Mr. R. Bodmer said that Mr. Richmond having stated that he considered it was the farmer who adulterated milk, and not the milkman, he must have a very high opinion of the retail London milkman. He was not speaking of large wholesale companies, but of little petty milkmen, who supplied poor districts, such as Bermondsey. Surely Mr. Richmond did not think that such a man was above putting water in milk, and, supposing he did, he would use London water, which contained such a small quantity of nitrates that the nitrate test would be quite useless. He wished to know what process the author of the paper adopted for determining milk sugar; and also how the ash was determined; whether he used a muffle or an argand burner. In one case he (Mr. Bodmer) was told that an analyst ignited his milks in a muffle at almost a bright-red heat, and naturally got only half the normal amount of ash.

Mr. Cassal, in view of the fact that most London waters contained, as a rule, about 0.18 parts per hundred thousand of nitrogen as nitrates, desired to ask Mr. Richmond whether, supposing that a milk had been adulterated to the extent of 10 per cent. with London water, containing that amount of nitrates, he was prepared to say that the test suggested by him would detect that amount. He observed, in reference to Mr. Richmond's remarks concerning the microscopic examination of milk, that, at one time, all the samples of milk which came into his laboratory were examined microscopically; and he might state that, in cases of extensive deficiency in fat, it was invariably found that the fat globules were all very small. In these cases of considerable deficiency in fat, the microscopic examination gave positive evidence of fat abstraction or deficiency by the smallness of their number, and of their size, so long as the examinations were made by the same person, and in the same way; but whether it was possible to found an invariably reliable test on this, he was disposed to doubt. He understood Mr. Richmond to suggest that microscopic examination might enable analysts to say definitely that fat had been extracted from milk owing to the absence of all large globules. He doubted whether a public analyst could go into court with such evidence. With regard to the nitrate test, it struck him (Mr. Cassal) as being a matter of the utmost importance, and very well worth working out, although the suggestion was by no means a new one. Several years ago Mr. Uffelmann suggested testing for nitrates in milk for the purpose of detecting added water. He believed that the proposition was received at the time with some doubt, not to say with some ridicule, a fact which was to be regretted. He did not think that the detection of the presence of nitrates in milk adulterated with London water to the extent of 10 per cent. should at once be put on one side as impossible. In the case which occurred recently in a London police-court, the so-called evidence for the defence could without much trouble have been proved to be

absolutely valueless; but the detection of anything which could be regarded as characteristic of extraneous water, beyond what was now relied upon, would plainly have been of great value in its effect on the magistrate's mind. He was glad that Mr. Richmond had alluded to the evidence given for the defence in that case, and that he had expressed his opinion that it was worthless. He (Mr. Cassal) would invite the Society to carefully consider the point that had been raised in a recent case in which a certain analyst, not a member of the Society, was called to give evidence on behalf of a vendor of milk alleged to be adulterated. This analyst was reported to have said that he had seen seventeen cows milked in a field, that he had analysed a sample of the mixed milk, and that if such a sample had reached him in the ordinary course he would have reported it as containing from 8 to 10 per cent. of added water. It was unfortunate that in the report of that case no statement was made as to whether this analyst was cross-examined with respect to the limit which he used, because it would have been perfectly possible to make an assertion of that description by taking a high standard; and he (Mr. Cassal) was disposed to believe that if that analyst had been so cross-examined he would probably have had to admit that the limit he used was not the same as that employed by the public analyst, who had certified the milk in dispute to be adulterated. But while public analysts would hail with all possible satisfaction any valuable addition to the methods employed for detecting the difference between added water and the water which is natural to milk, the position of the public analyst under the Sale of Food and Drugs Act in regard to milk was quite clearly defined, and was not affected by these so-called abnormal cases. The composition of the article which a purchaser was entitled to get when he asked for milk, was perfectly well-known from the hundreds of thousands of analyses of milk that had been made, and it was the duty of public analysts to point out that such abnormal samples as had been alluded to were not *milk*, either from a scientific, legal or public point of view. It was not the article required by the purchaser, but something totally different. It seems to be accepted in a loose kind of way by many persons that milk was anything which could be extracted from the udder of any cow. Such a definition was utterly unscientific and obviously worthless. The only possible definition was one founded upon the large number of analyses made of the normal article, which showed beyond all question what the composition of that normal article was. The results of analyses of abnormal fluids were certainly highly interesting in themselves—especially from a pathological point of view—but they did not affect the position of the public analyst at all, because such fluids were not milk in the scientific, legal or commercial sense. In the case alluded to by Mr. Richmond, viz., *Dyke v. Gower*, it was laid down by the High Court that milk must be sold whole by the milkman, and that the defence that the fat was deficient because the cream had risen in the can during the process of serving was no defence. It had, therefore, been definitely settled that the vendor of milk was responsible that the article he sold was what was demanded of him, and this dictum was clearly applicable to the case of watered milk, as well as to the case of fat abstraction. It was, in fact, the business of the producer or vendor of milk, or of any other article, to see that he sold the article that he was called upon to sell. In the recent case alluded to it was therefore plain that under the 6th section of the Sale

of Food and Drugs Act, an offence had been committed, and that a conviction should have followed. He could only express the hope that all public analysts would take up this position, which was, in fact, the only scientific and logical position, and would refuse to recognise as milk any of those abnormal fluids and disease-products, the composition of which had been on certain occasions laid before the Society. He desired, further, to express his deep regret that there were still persons to be found who were willing to give a certain type of evidence in Courts of Law.

Mr. Cecil H. Cribb mentioned that in a case in which he had recently been concerned he was asked, in conjunction with another chemist, to see eight cows milked, and to analyze samples of the milk from each afterwards. No less than twelve out of sixteen samples turned out to be abnormal, and it was interesting that in the case of one of the cows both the morning and evening milk gave figures below those obtained by Mr. Richmond. The figures being for the evening milk :

Total solids	...	...	...	...	...	...	...	11.01
Fat	...	...	...	...	...	...	...	3.54
Sugar and proteids	...	...	...	...	...	...	...	7.47
Ash	...	...	...	...	...	...	...	0.69
								8.16

The results of the rest of the abnormal samples varied between those just quoted and the normal. Without going into details then, though he would like to have the figures recorded in THE ANALYST, he observed that the relation between the ash and the solids-not-fat in all cases bore out Mr. Richmond's suggestion.*

Mr. E. J. Bevan said that he had tried the test mentioned by Mr. Richmond, but in a sample of what he had reason to believe was genuine milk he had certainly got a reaction for nitrates. He would like to ask Mr. Richmond whether nitrates might not often find their way into milk. In the case referred to by him he tested other milks side by side, and in these instances he obtained no reaction whatever, and he could only come to the conclusion, subject to the limited experience he had had in this particular test, that there were nitrates present in the milk which he had examined, and which he regarded as genuine. He admitted that if in testing a milk one got a very considerable reaction for nitrates, it might throw a good deal of suspicion on the sample. He observed that Mr. Richmond had not noticed any recent

* The following are the figures for each of the abnormal samples, the analyses of the morning and evening milk of the same cow being placed together :

Link of the same cow being placed together.							Ash x 100,
			Total Solids.	Fat.	S.N.F.	Ash.	S.N.F.
(1)	{ Morning	...	11.01	3.54	7.47	0.70	9.4
	{ Evening	...	11.16	3.73	7.43	0.70	9.4
(2)	{ Morning	...	10.97	3.06	7.91	0.73	8.8
	{ Evening	...	11.77	3.97	7.80	0.76	8.8
(3)	{ Morning	...	11.12	3.20	7.92	0.69	8.7
	{ Evening	...	11.54	3.80	7.74	0.69	8.9
(4)	{ Morning	...	12.16	4.04	8.12	0.70	9.2
	{ Evening	...	12.10	3.99	8.11	0.70	9.8
(5)	{ Morning	...	11.63	3.47	8.16	0.72	8.6
	{ Evening	...	12.33	4.16	8.17	0.72	8.6
(6)	{ Morning	...	11.89	3.42	8.47	0.69	8.1
	{ Evening	...	12.61	4.21	8.40	0.71	8.4

The cows were considered to be in their usual health. It was suggested that the change from the winter food (oil-cake, etc.), to fresh grass, which had recently taken place, was the cause of the poorness of the milk.

diminution in the amount of fat in normal samples. He was exceedingly pleased to hear this, because it entirely bore out the results of his own experience. He had tried to convince Mr. Plowden, one of the London magistrates, that no natural diminution had occurred, and offered to show him the results of analysis of 188 samples taken in July, August, and September. The average percentage of fat in these samples, which included both genuine and adulterated, was 3.6, and in the particular case in which he had to appear the percentage was 2.4. The magistrate refused to listen to any such arguments, or to look at any results, or take any further evidence, and the case was dismissed.

Mr. Hehner thought that until the nitrate test had been used by many analysts, and under a variety of varying circumstances, it would hardly be safe to rely upon it as a definite test for adulteration with water. The subject brought forward by Mr. Richmond was of the utmost importance. The way out of the difficulty suggested by Mr. Cassal—namely, that milk which, though unwatered, was not of the normal minimum composition, and should not only not be called milk, but that the sale of it should render the vendor liable to punishment under the Food Acts—would hardly at present commend itself to magistrates. In time Mr. Cassal might be able to educate the public to look upon milk as the normal fluid produced by healthy, well-fed cows, but as yet the time had not yet ripened for the criminal prosecution of persons selling abnormal, but unadulterated milk. Meanwhile, Mr. Richmond was looking upon the facts as they were, and had made a very gallant attempt to grapple with the question of abnormal milk. He (Mr. Hehner) thought, however, that he had hardly been successful. As to the suggestions just touched, but not insisted, upon by Mr. Richmond, concerning the size of the fat globules and the presence of deposits in centrifugals, he would say that the size of the fat globules did not depend upon the amount of skimming alone, but was materially influenced by the period of lactation in the cow. When a cow was in full milk the globules were comparatively large, but their size gradually diminished, until, when the end of the period of lactation approached, their size was very considerably reduced. It must be noted in connection with this that it was just towards the end of the lactation that cows gave the worst milk and the poorest butter, and that that was just the time when the difficulty of distinguishing between milk naturally poor and that artificially reduced in quality arose. With reference to the deposit in milk-separators, this, as far as he remembered, had first been mentioned by Mr. Faber at a recent meeting of the Society. Considering that Mr. Richmond had not made any determinations of the amount of this deposit, nor even ascertained its exact nature, it appeared to him (Mr. Hehner) extremely risky to found upon such indefinite knowledge such a proposal as Mr. Richmond had done.

As to Mr. Richmond's arguments founded upon various constituents of the solids-not-fat, the case was considerably stronger. The main contention advanced was that the amount of ash in genuine milk, however low in solids-not-fat that milk might be, was fairly constant. Mr. Richmond agreed with Dr. Vieth in this; the latter found that the ash bore a constant, or nearly constant, proportion to the percentage of caseine, while Mr. Richmond comes to the conclusion that in abnormally low milks the caseine is not much affected, but that it is the milk-sugar that diminishes. Or,

putting it in other words, the ash bore, in genuine milk, a fairly constant proportion to the amount of solids-not-fat, being about 8.3 per cent. of the latter, while in abnormally poor milks the percentage of ash to solids-not-fat was higher. Generally speaking, all this might be perfectly true, but it would not help the Public Analyst much in coming to a correct judgment; for it was in the samples containing about 8 to 10 per cent. of water where the difficulty of judging came in, and in these the ash was of very little definite help. Assuming a milk with 8.5 per cent. of solids-not-fat contained 0.73 per cent. of ash, then that milk watered down to 8.2 would still have 0.70 per cent. of ash. Mr. Richmond would argue that this milk must be genuine, as the ash was not materially deficient; and yet it had been artificially brought down from normality to exceptional and rare poverty. Mr. Richmond's argument from the constancy of the proportion of milk-sugar in normal milk was no stronger. He stated that normally the milk-sugar amounted to 53 per cent. of the solids-not-fat, with a variation of 2 per cent. either way. Considering that the total amount of milk-sugar in milk was only 4 per cent., and that milk-sugar was the constituent most liable to rapid diminution, and that our methods of estimating milk-sugar were hardly so perfect that a variation of, say, 0.2 per cent. would be an inexcusable error in analysis, that amount being the whole of the balance between milk-sugar in genuine, poor, and watered adulterated milk, it appeared to him far from safe to found upon this circumstance such a superstructure as Mr. Richmond had raised.

It thus came all back to the nitrate test, which must give a reaction with a milk low in solids-not-fat before such milk could be safely condemned. But Mr. Richmond admitted that he could not find by that test 10 per cent. of London water. It must, lastly, not be forgotten that, unlike Mr. Richmond, who could follow his samples back to the cow, the Public Analyst was not in that fortunate position, and had solely to rely on his analytical figures in giving a certificate upon a sample of milk. Would Mr. Richmond, were he in the position of the Public Analyst, have made the suggestions which he had brought forward that evening? At the same time, the society was thankful to the author of the paper, which, if not at present very practicable, was at least eminently suggestive.

Mr. Richmond, in reply, said that he was glad to hear Mr. Hehner's full and frank criticism, as many of the points raised by Mr. Hehner had occurred to him, and he was perfectly well aware, in bringing this paper before the Society, that it was a question of small differences and very careful determinations. Mr. Hehner's first objection was that the size of the fat-globules was affected by the stage of lactation. He was aware that, speaking from limited experience, the size of the large globules was affected; but it was the proportion of the very small ones which were not removed by separating milk, and upon this he thought an opinion might be based. He brought forward the idea in the hope that someone possessing time, patience, and microscopical skill would take it up. As far as his experience went, the proportion of the very small to the large was not very variable, but he would not like to give a positive opinion on the point. A complete micrographical study of milk even if it did not give results analytically useful, would be of the greatest value. With reference to the question of "separator slime," he would point out that Mr. Faber had said that it contained all the dirt of the milk, but did not state that it

consisted wholly of dirt. He could not think that Mr. Hehner had examined this substance. Certainly there was a layer of dirt, but there was a white layer on the top of this, and of course it was possible—he might be wrong in what he had stated—that the white substance might also be dirt. He had not examined it very fully, but all his results pointed to the presence of a substance which was not dirt. He still thought that this determination might afford evidence of adulteration. With regard to the evidence afforded by milk-sugar estimations—and this would also reply to Mr. Bodmer's question as to the determination of this substance—he distinctly stated that he did not lay very great stress upon it, chiefly because the methods of estimating the milk-sugar and proteids were not very exact; it was merely a corroborative test, but he did not think that it should be utterly rejected on that account. He knew that the difference of two-tenths of a per cent. was almost within the limits of experimental error, but he thought that with careful working, and if the sugar were determined by the polariscope, closer results might be attained; he did not think that it could be worked by other methods as accurately as with the polariscope. In doing his sugar determinations he exactly followed Dr. Vieth's procedure, with the exception that he used a correction for the polariscope, which Dr. Vieth had not done. Mr. Hehner's chief point against the evidence afforded by the ash was that if a milk contained 8.5 of solids-not-fat, and 0.73 of ash, and it was watered down to 8.2, the ash would be found to be 0.70. He (Mr. Richmond) would call 0.73 a high ash in a milk containing 8.5 per cent. solids-not-fat. He thought that the larger number of milks having 8.5 per cent. of solids-not-fat would contain less than that, and nearer 0.70 per cent. He would not pretend that he had come forward with methods which would absolutely detect every case of milk-adulteration, no matter what proportion of water was contained; but as all the evidence went to show that abnormally low milks contained a high ash, an analyst who found a milk with low solids-not-fat and low ash could give evidence that it had not the composition of an abnormal milk, should this be suggested by the defence. When estimating the ash he sometimes used an argand burner, and sometimes a muffle. He thought that the muffle was a piece of apparatus which was not sufficiently used in chemical laboratories, for by its means almost any temperature could be obtained. It was possible to ignite with a muffle at a very low temperature.

He had also used an argand burner when examining single samples, and in that case, as he had been very careful to avoid a red heat, he did not think his ash figures were under-estimated. He hardly ever found a difference of more than 0.02 per cent. in duplicate estimations. He had not intended to say that, by the proportion of ash to the solids-not-fat, all cases of watering could be detected, but he still believed that it would be a valuable determination in doubtful cases. He had already explained that the ratio of solids-not-fat to ash was, approximately, 100 to 8.3.

What he intended to say in connection with the farmer watering the milk was, that in the evidence given in courts the blame was always put upon the farmer, and this evidence would not be entirely untrue.

In reply to Mr. Cassal's question as to whether, supposing that a milk had been adulterated to the extent of 10 per cent. with London water containing 0.18 parts

per hundred thousand of nitrogen as nitrates, that amount could be detected by his process, he had not tried the experiment with London water, but should think that it was possible that the test might fail.

Mr. Bevan's observation that the nitrates might occur in milk, differed from his own, but he had no hesitation in accepting the statement. He would not like to indulge in any theories as to whether the cow had drunk water containing nitrates, or whether it had eaten roots, or anything else. All the milks which he had examined came from farms in which the water was good, and the quantity of nitric acid was extremely small.

[NOTE.—Since reading the paper I have had given to three cows one gramme of potassium nitrate per day in their food for three days; eight hours after the last dose of potassium nitrate was administered, the cows were milked, and the milk gave a strong reaction for nitric acid; twenty hours after the last dose the cows were again milked, and the reaction for nitric acid, though not so strong, was quite distinct. As I have on several occasions found on farms waters containing from 10 to 15 parts per 100,000 of nitric acid, a quantity equal to one gramme of potassium nitrate might easily be absorbed daily by the cattle. Mr. Bevan's observation and my own render it necessary to discard the "nitric acid test" for water in milk.—H. D. R.]

The remaining paper was :

ON THE EXAMINATION OF COPPER SULPHATE.

By JOHN RUFFLE, F.I.C., ETC.

THE increasing employment of copper sulphate as a vine-dressing for the phylloxera, and as a preventive dressing for potato disease, directs more attention to the analysis of commercial copper sulphate.

The usual good qualities, as found in the market, are sold on a guarantee of 98 per cent., and contain only traces of iron and other metallic impurities; the lacking 2 per cent. is made up by a little free sulphuric acid from the mother liquor, which remains imprisoned between the crystals, and moisture left behind through a more or less incomplete drying of the crystals after washing.

To arrive at the true amount of copper sulphate, take 1 to 2 grammes, dissolve in water, neutralize with ammonia, make up to from 300 c.c. to 400 c.c. with water, and acidulate with about 3 grammes of sulphuric acid, adding this, of course, in a diluted state. Turn on a steady electrical current from any battery, but of such strength as will give 20 c.c. to 50 c.c. of electrolytic gas per hour, employing platinum anode and cathode. Leave over-night, wash cathode with water and absolute alcohol, dry, cool, and weigh. The larger the cathode surface, within reasonable limits, the better, a brighter and more compact deposit being thus obtained. A total cathode area of about 20 square inches answers well for the deposition of up to 0.5 gramme of Cu. Calculate the Cu obtained into $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

For the free acid, take 20 to 50 grammes of the crushed crystals, stir well with successive portions of absolute alcohol, add water to the alcoholic extract, a few drops

of phenol-phathlein solution, titrate with standard soda, and calculate into free sulphuric acid.

The determination of the excess of water or "moisture," though at first sight apparently an easy operation, is not really so, and cannot be done by any one known method. Experiments made to discover the readiest way of estimating the "moisture," show that :

First, the true amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ present must be found.

Second, a portion must be dried at a temperature of 100°C ., to constant weight, and the loss noted.

To effect this second point, take 3 to 5 grammes of the crushed sample, expose to 100°C . for two hours, cool, and weigh. The loss will be the excess of free water, plus the amount of water of crystallization due to four out of the five molecules of water in the true amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ present.

The loss of $4\text{H}_2\text{O}$ at 100°C . in pure 100 per cent. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is 28.91 per cent.* If the percentage be not 100, but only 98, the loss therefrom would then be only 28.33 per cent., and if the total loss at 100°C . were, say, 29.50 per cent., this, minus the 28.33, would leave 1.17 per cent. difference as the amount of "moisture."

This procedure of determining the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, as well as drying at 100°C ., is an unavoidable double operation, since experiments show that no known method can be employed to effect the "moisture" determination without encroaching more or less upon the four molecules of water of crystallization. These seem to be held very loosely, whilst the fifth is retained with great tenacity.

Two examples of excellent high-class copper sulphate, treated as above, will show the results obtained, the one being a sample of wet, undried crystals, the other of crystals dry and ready for casking :

	Wet.		Dry.
Copper found by electrolysis	24.52		24.90
Total loss at 100°C	30.60		29.42
Less that due to $4\text{H}_2\text{O}$ at 96.94 per cent....	28.31	at 98.42 per cent.	28.45
	2.29		.97

giving :

	Wet.		Dry.
Crystals $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	96.94		98.42
Moisture	2.29		0.97
Free H_2SO_4	0.68		0.49
Undetermined and loss	0.09		0.12
	100.00		100.00

If examined minutely, the copper sulphate crystals will be found to contain traces of many of the metallic impurities which existed in the copper originally employed ; the principal of these is generally iron, but if the copper were auriferous or argentiferous, the gold or silver would be respectively detected in the crystals.

As illustrating the difficulty found in estimating the "moisture" alone, some

* Taking $\text{Cu} = 63$, $\text{O} = 16$, $\text{S} = 32$, $\text{H} = 1$.

experiments made may be quoted. Two portions of each of the foregoing "wet" and "dry" samples were exposed to the drying action of strong sulphuric acid under an air-pump, and the loss of weight incurred noted until constant. Constancy was reached in about six weeks, the final loss in each case being:

Loss over sulphuric acid under air-pump:

						Dry.		Wet.
1st sample	...	...	...	...	...	30.22	...	29.43
2nd sample	...	...	...	...	...	30.31	...	29.38

The same was done in presence of freshly-fused calcium chloride, in about the same time.

Loss over fused calcium chloride under air-pump:

						Wet.		Dry.
1st sample	...	...	...	...	...	29.83	...	29.20
2nd sample	...	...	...	...	...	29.83	...	29.23

Dehydrated copper sulphate, dry sodium chloride and dry sodium nitrate tried in a similar manner all gave imperfect results.

It is interesting to notice and contrast the total loss at 100° C. with that over the sulphuric acid and calcium chloride, both being at the ordinary temperature of the air.

				Loss at 100° C.		Loss over H ₂ SO ₄ .		Loss over CaCl ₂ .
"Wet"	...	...	...	30.60	...	30.22	...	29.83
						30.31		29.83
"Dry"	...	...	...	29.42	...	29.38	...	29.20
						29.38		29.23

For the low qualities of crystals, it is only necessary to determine the copper, and calculate this into $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Dr. Sykes exhibited a small gas boiling burner, which had been forwarded to him in his official capacity by Messrs. Fletcher and Co., of Warrington. It was intended to illustrate a method of enamelling recently introduced by that firm, who state that the covering applied will withstand exposure to a red heat for any length of time, that it does not chip off, and that it is practically indestructible. The enamel can be applied in any shade, colour, or variety of colours. He (the speaker) suggested that a very useful application of this invention would be the enamelling of the iron parts of apparatus used in the laboratory, for, with the varnish at present employed, such parts became very unsightly after being in use for some time.

(Conclusion of the Society's proceedings.)

The Analysis of Sperm-oil containing Mineral-oil. C. A. L. de Bruyn (*Chem. Zeit.*, 1893, xvii. 1453).—The rough qualitative test of the presence of mineral-oil in sperm-oil—consisting in saponifying a small quantity with alcoholic potash, diluting the liquid with water, and observing the separation of unsaponified mineral-oil—is not interfered with by the presence of cetyl alcohol and its congeners in normal sperm-oil, as these bodies are retained in suspension in the soap solution and only separate on standing. The accurate determination of mineral-oil in an adulterated

sample of sperm-oil can be effected by the usual method of saponification, followed by extraction of the soap solution with an immiscible solvent, and treatment of the resulting mixture of higher alcohols and mineral-oil with acetic anhydride. In carrying out this separation, the mixture of mineral-oil with higher alcohols is boiled for half an hour with double its volume of acetic anhydride. Complete solution takes place, but the mineral-oil separates again on cooling. The two layers are separated and the mineral-oil freed from acetic anhydride by washing with dilute alkali. The higher alcohols, which are obtained as esters on adding water to their solution in acetic anhydride, can be recovered and their amount determined.

The author points out that it would be desirable to know whether the percentage of higher alcohols is sensibly constant in pure sperm-oil. B. B.

NOTE BY ABTRACTOR.—The abstractor has found a nearly constant percentage of 40 per cent. of higher alcohols in pure sperm-oil; variations are often due to incomplete extraction rather than difference in composition.

The Acidimetric estimation of Potassium Borofluoride. F. Stolba. (*Casopis pro prumysl chemicky*, 1893, iii. 298; through *Chem. Zeit.*)—The principle of the method consists in the decomposition of potassium borofluoride by fusion with sodium carbonate according to the equation:



A weighed quantity of the borofluoride in a finely-powdered state is heated in a deep platinum crucible with about four times its weight of sodium bicarbonate, which is preferable to the carbonate, as it can be weighed more exactly. The quantity of sodium bicarbonate taken must be accurately known, as the estimation of the borofluoride is effected by means of the loss of alkalinity of the melt. When fusion is complete, and the escape of carbon dioxide has ceased, the contents of the crucible are dissolved in water in a capacious platinum dish, and the solution heated to boiling and titrated, using litmus as an indicator, and taking care to avoid the addition of much acid at one time, lest the borofluoride be re-formed. The presence of boric acid is said not to interfere. The alkalinity of the bicarbonate used must, of course, be determined.

B. B.

Critical Examination of Methods for the Estimation of Sulphur. L. Marchlewski. (*Zeit. anal. Chem.*, 1893, xxxii. 403; through *Chem. Zeit.*)—Gröger's method, which consists in heating the pyrites with metallic iron to convert it into ferrous sulphide, treating the latter with hydrochloric acid in a current of carbon dioxide, and absorbing the hydrogen sulphide in a solution of iodine of known titre, is inadmissible because any sulphates which may accompany the mineral are partially reduced to sulphides during the ignition with iron. With pure sulphides the method gives good results; for sulphates it is useless, inasmuch as reduction is never complete. Sauer determines the sulphur by burning the pyrites in oxygen, passing the sulphur dioxide into bromine water, and determining the sulphuric acid there produced; this can be recommended as far as the agreement of results is concerned, but is troublesome, and must give place to Lunge's method unless soluble sulphates be

present. Föhr's method, wherein the hydrogen sulphide obtained by suitably decomposing the mineral is absorbed in an ammoniacal solution of zinc sulphate, ferric sulphate (and presumably acid) added to the liquid containing the zinc sulphide, and the ferrous sulphate produced titrated with potassium permanganate, is not capable of yielding accurate results. Klobukow also recommends evolution of the sulphur as H_2S , using nascent hydrogen for the purpose, and absorbing this in iodine solution of known titre; this process is inadmissible, on the same grounds as those which render Gröger's method useless.

A. G. B.

The Oxidation of Fatty Oils. W. Fahrion. (*Chem. Zeit.*, 1893, xvii. 1453, 1454.)—Sundry attempts have been made from time to time to determine directly the increase in weight of fatty oils allowed to oxidize in the air; various plans to expedite the rate of oxidation having been adopted. Thus Livache carried out experiments in which the oil was allowed to fall on finely-divided lead; while Vogel, more than thirty years ago, proposed cotton-wool as a support for the oil. The author has found that chamois-leather is more suitable for the purpose than either of the materials mentioned. It is, however, somewhat hygroscopic, and a blank experiment must be carried out at the same time as those with the oils, to correct for its changing content of water as nearly as possible.

Oil.	Iodine number.	Days' exposure.	Maximum gain.
Olive ...	82.1	42 ...	0.2%
Sesame ...	110.2	21 ...	3.6
Rape ...	102.4	10 ...	2.8
Cotton-seed ...	109.2	10 ...	5.6
Poppy ...	135.9	7 ...	8.4
Walnut ...	149.2	6 ...	9.0
Linseed ...	175.8	6 ...	12.4
Cod ...	171.0	5 ...	9.5

The number of days' exposure is the length of the period that elapsed before the full gain in the weight of the oils under test took place. A longer exposure does not necessarily increase the weight of an oil suffering oxidation, as volatile products, such as carbonic, formic, and acetic acids, may be formed. It is worthy of note that the iodine absorption of an oil does not give an accurate estimate of its power of absorbing oxygen. This becomes evident on converting the iodine numbers given above into their oxygen equivalents, and comparing the figures thus obtained with the oxygen absorbed, determined directly. This is due to the fact that, instead of the mere addition of an oxygen atom to an unsaturated compound, the insertion of an atom between adjacent atoms of carbon and hydrogen and the formation of an hydroxyl group may take place. Moreover, oleic acid, which absorbs iodine, does not readily take up oxygen, so that a discrepancy between the iodine and oxygen absorbed will be apparent in all oils containing oleic acid.

B. B.

Reactions of Hydrazines with Lignin. E. Nickel. (*Chem. Zeit.*, 1893, xvii. 1209 and 1243.)—Phenylhydrazine hydrochloride may be used as a reagent for lignin, the aldehydic nature of which has been demonstrated, as follows: In an aqueous solution of phenylhydrazine hydrochloride wood acquires a light yellow

colour, which becomes deeper on addition of dilute hydrochloric acid (about 15 per cent.). When the sample is set aside the yellow colour changes to a pure green in the course of an hour, or longer.

Hydrazine sulphate (now obtainable from Kahlbaum) gives a very similar reaction with wood. In a cold solution of this salt the wood becomes yellow in a few minutes, the depth of colour depending on the nature of the wood, and attaining its maximum with bamboo-cane, among the woods which the author has examined. The subsequent action of 20 per cent. hydrochloric acid on the wood changes the yellow to orange.

It is characteristic of aromatic aldehydes to give colour-reactions with the hydrazines, and the above behaviour of wood might be due to the aromatic aldehydes which it is said to contain, namely, vanillin and cinnamyl aldehyde. An aqueous alcoholic solution of vanillin yields a yellow colour with hydrazine sulphate, and, on the addition of hydrochloric acid, a yellow precipitate falls, but there is no orange colour produced. The author has already denied that these aldehydes are constituents of wood, and he regards the above reaction of vanillin as confirmatory of his views.

A. G. B.

Valuation of Leather Glue. F. Gantter. (*Zeit. Anal. Chem.*, 1893, xxix., 413; through *Chem. Zeit.*)—One hundred grammes of the shredded sample are heated with 1 litre of water containing a few drops of caustic soda solution until solution is complete, when the volume of the liquid is made up to 2 litres. After the solution has been set aside for ten hours, 20 c.c. (= 1 gramme of glue) of the clear liquid are evaporated, and the residue is dried at 105°, weighed and ashed. The weight of the ash-free raw glue is thus ascertained.

To estimate the pure glue in the sample, 20 c.c. of the above solution are transferred to a 100 c.c. cylinder, diluted with 30 c.c. of water, and neutralised with acetic acid. Tannin solution is then added, until no further precipitation occurs; the solution is shaken, made up to the mark with water, and filtered through a dry filter. The filtrate is shaken with hide powder, and set aside for ten hours to ensure complete elimination of tannin. After another filtration 50 c.c. of the solution are evaporated, and the residue dried, weighed, and ashed. By subtracting the weight of this residue, less that of the ash, from the weight of the ash-free raw glue, the percentage of pure glue substance is ascertained.

A. G. B.

Butter Distinguished from Margarine. F. Gantter. (*Zeit. Anal. Chem.*, 1893, xxxii. 411; through *Chem. Zeit.*)—The frequent occurrence of earth-nut oil in margarine renders the identification of the latter in butter an easy matter. Butter containing so little as 1 per cent. of earth-nut oil will give a dark brown-red colour when treated with concentrated sulphuric acid (ANALYST xviii. 183); pure butter should give a straw-yellow or reddish-yellow colour. The iodine number of butter-fat, as determined by the author's method (employment of a chloroform solution of iodine instead of Hübl's solution) should be between 13 and 16; that of earth-nut oil is 49-51.

A. G. B.